

**HIGH-ENERGY LASER DIAGNOSTICS FOR REAL-TIME  
MEASUREMENTS OF DIESEL PARTICULATE MATTER EMISSIONS**

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**INTRODUCTION**

Particulate matter (PM) emissions from diesel engines have been reduced by more than an order of magnitude since the inception of mandated emission regulations, and an additional order-of-magnitude reduction will be required in the U.S. beginning in 2007. The tremendous improvements achieved to date are the result of a large reduction in the size of emitted particles, but at the expense of a large increase in their number. The contemporary, "visually clean" heavy-duty diesel engine produces 3-4 orders-of-magnitude more small particles than its "smoking" predecessor. This dramatic change in the character of PM emissions has created two new problems: first, the health risks are believed to be greatly increased, because small particles penetrate far deeper into the lungs where they have a much higher probability of remaining; second, because both the size and mass of PM emissions have been reduced by so much, it has become more difficult to make accurate measurements, particularly when using the U.S. Environmental Protection Agency (EPA) mandated gravimetric procedure of filter weighing. In addition, as engine exhaust becomes cleaner the PM emissions during transient operation constitute a greater percentage of the total PM measured during the emission driving cycles.

A consequence of this evolution in PM emissions is a pressing need for improved instrumentation for its measurement, particularly with regard to increased sensitivity and temporal response. This paper describes three laser-based diagnostics that have been successfully applied to the measurement of diesel PM emissions - laser-induced incandescence (LII) for the solid carbon fraction, laser-induced desorption with elastic laser scattering (LIDELS) for the volatile fraction, and laser-induced breakdown spectroscopy (LIBS) for the ash.

**NATURE OF DIESEL PARTICULATE MATTER**

The U.S. EPA has defined PM by virtue of the procedures they have specified for the measurement of engine emissions, as any material deposited on a teflonated fiberglass filter from dilute exhaust gases sampled at a temperature below 51.7 °C. Thus, in addition to elemental carbon (EC), or soot, PM may also include condensable materials such as sulfuric acid or high boiling point hydrocarbons. It is not supposed to include measurable amounts of water. The generally accepted model of engine particulate matter is that it consists of a solid fraction, a soluble organic fraction (SOF), and sulfates. The adjective "soluble" comes from the analytic technique used to extract the organic fraction from the carbonaceous material. The SOF and sulfates are often combined into a single component, the volatile organic fraction (VOF), that can constitute as much as 50% of the PM mass.

The solid fraction is mostly elemental carbon with a density of approximately 2 g/cc. Morphologically, it consists of small, nearly-spherical primary particles 20-50 nm in diameter. These primary particles cluster into chain-like aggregates that can have widely varying sizes. Additional solid material occurs in the form of metal ash compounds derived mainly from lubricating oil.

The SOF consists of organic compounds with a density of about 0.8 g/cc. This includes the polycyclic aromatic hydrocarbons (PAH) that are a possible carcinogen and the major cause for the health risk fears of nanoparticle emissions from diesel engines. Most of the SOF in PM is absorbed onto the sur-

face of the primary particles, where it resides in the form of a thin outer shell. The source of approximately 75% of the SOF is lubricating oil.

The sulfate content of PM is mainly hydrated sulfuric acid that is derived from the fuel sulfur. The propensity of hydrated sulfuric acid to nucleate is believed to be the main source of the nanoparticles that appear during dilution. Once formed, they act as condensation sites for the absorption of unburned hydrocarbons. These small particles are generally free of EC.

#### LASER-INDUCED INCANDESCENCE

LII has been used for many years to study laboratory flames and diesel combustion, but only more recently has it been used for the measurement of exhaust PM<sup>1-8)</sup>. The technique uses a high-energy, pulsed laser beam to rapidly heat aerosol particles from the local ambient temperature to the carbon sublimation temperature ( $\sim 4000$  K). The emitted light (i.e., thermal radiation) is proportional to the volume concentration of EC in the PM. Neither cooling nor dilution of the exhaust gases is required, so measurements can be made either *in situ* or by continuous sampling through an external optical cell. A clean-air purge is required to keep the windows of an optical cell from becoming soiled, but this is easy to accomplish and results in a system that can be run continuously without a dedicated operator, which is a big advantage of LII over most other PM measurement techniques.

LII has a well-defined but complex response to volatile particulate matter. It is insensitive to liquid particles, because they absorb a negligible amount of laser energy compared to EC. For carbon particles coated with volatile material, the latter is believed to vaporize early in the laser heating period. Ash may also be present at low concentrations, and it is unknown whether it survives the high temperatures. In general, however, it is commonly assumed that the contribution from ash is negligible, and that LII measurements are representative of the volume fraction of EC matter in the exhaust.

Shown in Fig. 1 are measurements of typical laser-pulse and LII signals. The laser pulse width of 3-4 ns (full width at half maximum) is characteristic of compact Nd:YAG lasers. The LII signal rises to a maximum approximately at the end of the laser pulse, and then decays in a near-exponential fashion. The decay is due to conductive heat loss that persists for several microseconds, and can be used to estimate the size of the primary particles in an aggregate. The maximum in the LII signal is proportional to the EC volume concentration.

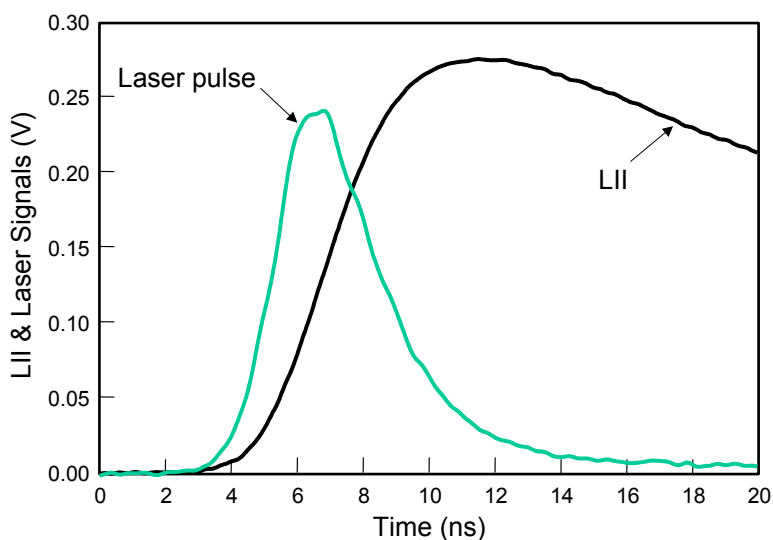


Figure 1: Typical laser pulse and LII signal.

The LII technique is well suited for real-time measurements during transient vehicle operation, making it an ideal tool for optimizing engine PM emissions performance. The measurement frequency is ultimately limited by the repetition rate of high-power pulsed lasers, which is typically 10-30 Hz, corresponding to one measurement per engine cycle at 1200-3600 rpm. In general, this is more than suffi-

cient to resolve the transients encountered in both the light- and heavy-duty Federal Test Procedure (FTP) driving cycles. Typical LII measurements for the light-duty FTP are shown in Fig. 2.

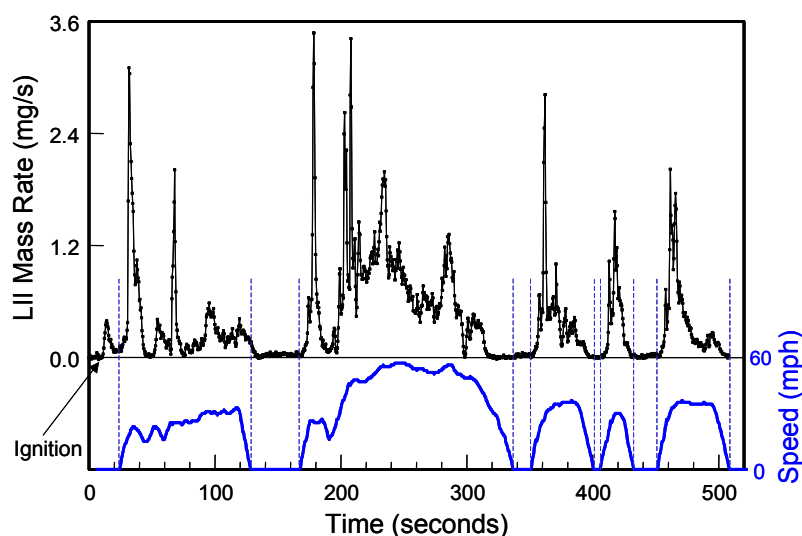


Figure 2: LII measurements for the cold start phase of the light-duty FTP drive cycle<sup>9)</sup>.

#### LASER-INDUCED DESORPTION WITH ELASTIC LASER SCATTERING

As mentioned earlier, as much as 50% of diesel PM can occur in the form of condensed volatile material. Abbass et al.<sup>10)</sup> have reported a comprehensive review of the more commonly used methods for measuring the non-solid fraction of PM, including vacuum-oven sublimation and thermogravimetric analysis for volatiles and Soxhlet extraction for solubles. These techniques typically require several hours or longer to obtain results, and none are capable of time-resolved measurements. LIDELS<sup>11)</sup> is a new technique that can measure VOF at the 10-30 Hz rates of high-energy pulsed lasers.

Double-pulsed LIDELS uses two laser pulses of approximately equal energy, separated in time by an interval long enough to permit completion of the physical processes associated with laser-induced desorption of the volatiles. The first pulse yields an ELS measure of the initial, total PM, and deposits the energy needed to desorb the volatiles. The second pulse ELS gives the EC volume remaining following desorption, and the ratio of the two measurements is the solid volume fraction. The limiting criteria for LIDELS is that the separation interval between pulses must be short enough to freeze the flow field in the probe volume. This condition can be satisfied by externally triggering the Q-switch of a standard pulsed laser twice during each firing of the flash lamps. For our laser we have found that a 150  $\mu$ s delay will yield two pulses with a total energy of approximately 25% of the normal, single-pulse output of the laser.

While there has been considerable research on the refractive index of “dry” soot, little is known about the effect of volatile-matter coatings on the scattering properties of diesel PM. In addition, the effect on scattering of a vapor cloud surrounding a particle, created in nanoseconds, is similarly unknown. Because of these uncertainties, it is assumptive to attribute all changes in light scattering efficiency from laser heated particles to be the result of volume change. However, we believe that true volume loss is the major contributor to the change in scattering intensity for the two laser pulses.

LIDELS measurements for an engine load sweep are shown in Fig. 3. The utilization of exhaust gas recirculation (EGR), as specified by the engine control module, is indicated in the figure with EGR in use for loads less than approximately 70 Nm. Note that the slope for the total PM is considerable larger than for EC when EGR is in use, and that the opposite occurs when the EGR is turned off. The solid fraction measurements in Fig. 3 reveal a distinct minimum of 0.72 at the load point where the

EGR was turned off. At the lowest load, with EGR, the solid fraction is 0.86, and at the highest loads the data asymptote to 0.96.

Because sub-nanosecond resolution is required to measure the scattered light intensity, the total PM and EC measurements shown in Fig. 3 were measured sequentially, each averaged for 30 seconds using a digital oscilloscope. Time-resolved LIDELS measurements require either a single laser and two oscilloscopes, or two lasers with collinear beams (e.g., a particle-image-velocimetry (PIV) laser) and a single oscilloscope.

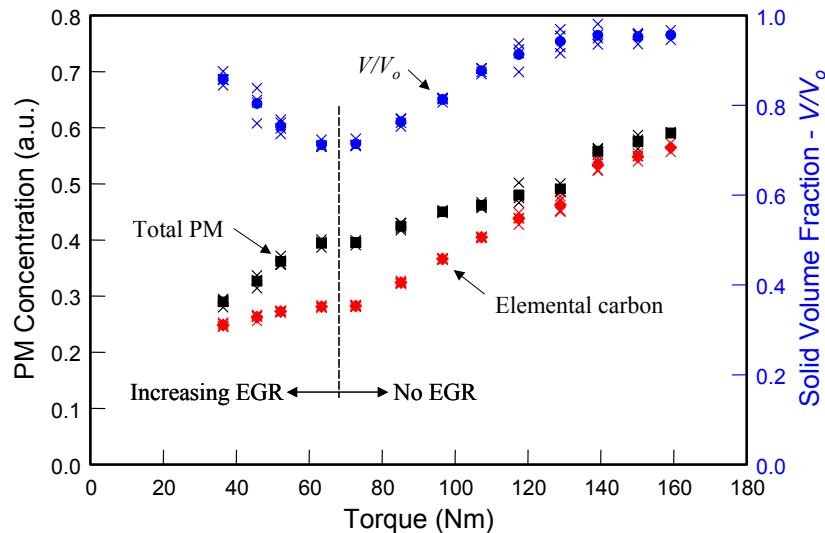


Figure 3: LIDELS measurements as a function of engine load<sup>11</sup>.

#### LASER-INDUCED BREAKDOWN SPECTROSCOPY

LIBS is a reasonably well-established experimental technique for the measurement of atomic species (solid, liquid, or gas)<sup>12,13</sup>. Measurements have been reported for metallic elements in the exhaust of a stationary, natural-gas-fired spark-ignition engine<sup>14</sup> using a portable monitoring system<sup>15</sup>. Because metallic ash has a detrimental effect on the long-term performance of diesel particulate filters (DPF), LIBS would appear to have potential value as a diagnostic for real-time, *in situ* measurements of ash entering a DPF. Of particular interest would be the measurement of input conditions for the life-cycle modeling of engine aftertreatment systems. Because several ash species are unique to lubricating oil, LIBS can also provide a measure of oil consumption due to oxidation; unfortunately, because oil is also consumed by evaporation, leaving the metallic additives behind, LIBS cannot provide a measure of total oil consumption.

Unlike LII and LIDELS, where a collimated laser beam is used to heat the soot particles, LIBS uses a focused laser beam to create a plasma. Breakdown occurs at the focus because the electric field exceeds the dielectric strength of the sample (and not because of selective absorption by a specific atom or molecule). Once breakdown occurs, the resulting plasma is highly absorbing and rapidly grows toward the laser with a conic shape. At early times, as the plasma cools the excited electrons and ions relax back to their ground states, emitting light dominated by a continuum due to the free electrons and ionic spectra characteristic of the species in the sample. As time progresses and the continuum continues to decay, however, certain long-lived excited species begin to appear as distinct lines in the spectra, leading to the often-used acronym of TRELBS (time-resolved LIBS). Because the decay rates vary widely for different species, optimization of the LIBS technique must be performed for each specific application.

Presented in Fig. 4 is a LIBS spectra for diesel exhaust, revealing the strong line for neutral calcium at 422.7 nm, and two lines for singly-ionized calcium at 393.4 nm and 396.8 nm. Calcium is the most

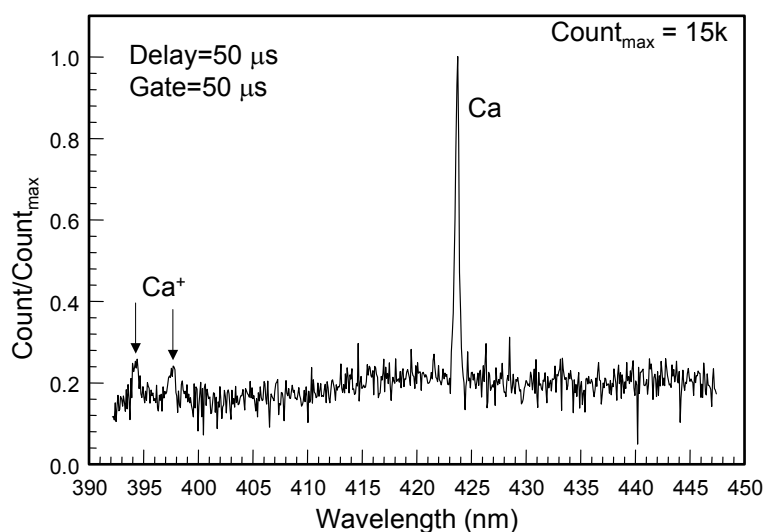


Figure 4: LIBS spectra for diesel exhaust, showing calcium lines from lubricating oil.

abundant metal in standard lubricating oil. This spectrum was obtained with an intensified CCD camera triggered 50  $\mu$ s after the laser pulse, with a gate width of 50  $\mu$ s. To make time-resolved LIBS measurements of calcium, the analog signals from two photodetectors would be recorded during the same time period as the camera gate, one with a narrow bandpass filter at 422.7 nm for the neutral calcium line, and the other at perhaps 417 nm for the background continuum.

#### SUMMARY

Of the three high-energy laser diagnostic techniques presented, LII and LIBS have matured to the point where commercial instruments are available. In contrast, LIDELS is still in the early stages of development, and much work remains before a robust, user-friendly, quantitative instrument will be produced. In general, elastic scattering measurements are more difficult than LII and LIBS because of a much lower signal-to-noise ratio, and the need for sub-nanosecond signal acquisition and greater dynamic range (LII is proportional to volume, whereas ELS is proportional to volume-squared). In addition, too little is known about the scattering properties of coated particles to enable quantitative ELS measurements of diesel PM emissions at this time.

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